

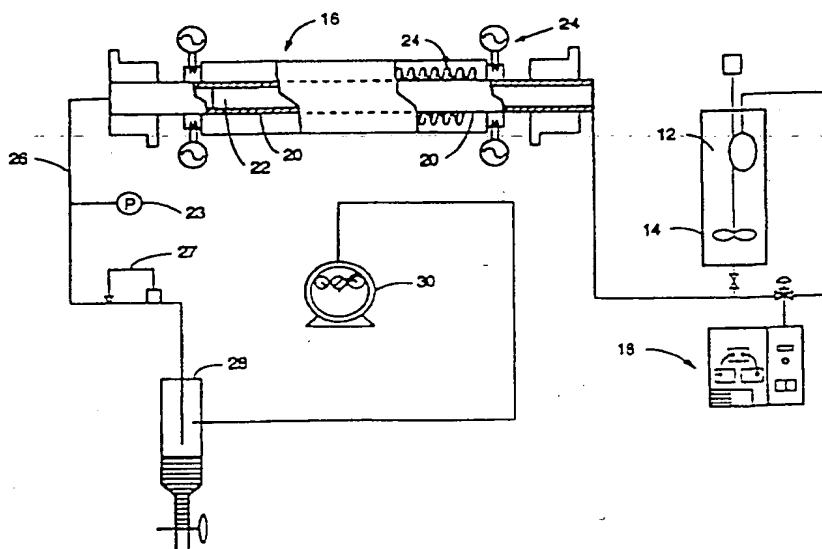
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C10J 3/00	A1	(11) International Publication Number: WO 96/30464 (43) International Publication Date: 3 October 1996 (03.10.96)
(21) International Application Number: PCT/US96/04439 (22) International Filing Date: 28 March 1996 (28.03.96) (30) Priority Data: 08/414,523 31 March 1995 (31.03.95) US (71) Applicant: UNIVERSITY OF HAWAII [US/US]; Suite 280, 2800 Woodlawn Drive, Honolulu, HI 96822 (US).	(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).	
(72) Inventor: ANTAL, Michael, J., Jr.; 357 Opihikao Place, Honolulu, HI 96825 (US). (74) Agents: JAMES, Patricia, Coleman et al.; Limbach & Limbach L.L.P., 2001 Ferry Building, San Francisco, CA 94111 (US).	Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: CATALYTIC SUPERCRITICAL GASIFICATION OF WET BIOMASS



(57) Abstract

A method for catalytically decomposing organic matter in a reaction medium is presented. Virtually complete gasification is achieved in relatively short periods of time. A hydrogen-rich gas may be formed from feedstocks (12) that include wet biomass, such as water hyacinth or algae, or organic waste or mixtures of biomass and organic waste. The reaction is catalyzed by a carbon-containing catalyst (22). The reaction medium may include supercritical water and is substantially oxygen-free. The carbon-containing catalyst (22) is stable in the environment of a supercritical water medium and maintains activity over long periods of time. Suitable carbon-containing catalysts are activated carbons or charcoals. Reaction products (26) are substantially free of tars or chars.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

CATALYTIC SUPERCRITICAL GASIFICATION OF WET BIOMASS

BACKGROUND OF THE INVENTION

Hydrogen has enormous potential as a fuel
5 source, due to its high energy value and cleanliness,
if it can be produced economically. Hydrogen is also
a very useful chemical reactant.

Conventional methods for generating hydrogen
include steam reforming of natural gas and
10 electrolysis of water. Improvement of these
conventional methods is desirable to avoid continued
reliance on uncertain and expensive supplies of
natural gas, increase efficiency of hydrogen
production and reduce energy consumption.

Another potential source of hydrogen under study
15 is biomass. Generally, biomass exists in the form of
terrestrial or marine plants as well as some
agricultural, industrial or municipal wastes. More
specifically, it has been contemplated to derive
20 hydrogen and other gaseous products through
thermochemical conversion of biomass. For example,
it is known that hydrogen and other gases are
produced from steam pyrolysis of cellulose at
atmospheric pressure. However, hydrogen yields have
25 been too low to make such a conversion process
commercially practical. In addition, conversion of
carbon in the biomass feedstock to carbon in the
gaseous product is relatively inefficient because, at
conventional operating conditions, refractory tar and
30 char are formed. These byproducts are also
undesirable since they must be removed from
processing equipment periodically.

Also, operating conditions in conventional
thermochemical conversion techniques such as

oxidation or pyrolysis have limited the hydrogen generated to an amount that is substantially less than that predicted from thermodynamic equilibrium considerations. Moreover, reaction rates have been too slow for commercial exploitation as a means for hydrogen production.

To date, wet biomass, that is, plants with a high moisture content, such as water hyacinth, banana tree, cattails, green alga, and kelp, though plentiful, relatively inexpensive, and renewable, has not been considered useful feedstock for such thermochemical conversion techniques. In large part, the disadvantage of wet biomass is the high cost of water removal often required before thermochemical conversion can be carried out. Also, the variety of carbohydrates and other chemical species in these plants and the number of mechanisms through which they can react have obscured understanding of the means by which wet biomass may be most efficiently decomposed to form the desired gaseous products without tar or char byproducts.

Efforts to increase the efficiency of hydrogen production and reduce generation of undesirable residues have continued. Particular attention has been given to the many carbohydrates that compose biomass using the reaction chemistry of glucose as a simple model. For example, glucose (about 0.1 M) has been completely gasified without a catalyst to mostly hydrogen and carbon dioxide in about 30 seconds at 600°C and 34.5 MPa. Higher concentrations of glucose (up to about 22% by weight) have evidenced lower conversion to hydrogen, carbon dioxide and hydrocarbons without a catalyst.

Studies from work in destruction of hazardous organic wastes have shown that carbon dioxide is produced from carbon monoxide at 500°C via the water

gas shift reaction in supercritical water. While this reaction plays a role in the production of hydrogen and carbon dioxide from glucose pyrolysis in supercritical water, much remains unknown about the pyrolysis of other carbohydrates in supercritical water since, at the high temperatures used for hazardous waste destruction, carbohydrates undergo many kinds of reactions, including dehydration and fragmentation, to form numerous species with a variety of reactivities.

Dairy waste has been converted in a supercritical water medium, at temperatures between 400°C and 450°C and pressures as high as 34.5 MPa, over catalysts containing alkali carbonates and nickel into a methane-rich gas.

In downdraft biomass gasification reactors, air containing tars and oils is directed downwardly past a fixed bed of carbon in order to crack out the tars and oils. Conventionally, for these techniques, the temperature is about 1000°C and pressure may be subatmospheric to about 4 MPa.

Accordingly, it is an object of the present invention to provide a method for converting organic matter such as biomass or organic waste to desirable products without the need for drying prior to treatment. It is another object of the present invention to provide a method for gasifying biomass or other organic matter that achieves a high efficiency of conversion of the organic matter to desirable gaseous products, and particularly hydrogen, at economical rates. It is yet another object of the present invention to achieve a high degree of gasification using an inexpensive, stable catalyst. An additional object of the present invention is to gasify concentrated organic matter feedstocks to hydrogen, methane and other simple

hydrocarbons. A further object of the present invention is to destroy organic waste efficiently and completely.

SUMMARY OF THE INVENTION

5 The present invention achieves these and other objects by catalytically decomposing organic matter, ~~such as wet biomass and organic waste, in a reaction~~ medium, producing a hydrogen-enriched product and substantially no tar or char residues.

10 In one aspect, the present invention provides a method that includes contacting a feedstock in a reaction medium with a carbon-containing catalyst for a time sufficient to gasify the feedstock, wherein the feedstock includes organic matter and the medium
15 includes water at a pressure of 22.1 MPa or greater and a temperature of 374 °C or greater. The catalyst may be an activated carbon or a charcoal.

 In another aspect, the present invention provides a method in which a carbon-containing
20 catalyst is provided in a reaction zone in a reactor, preheating and pressurizing the reaction zone, introducing a water-containing feedstock into the preheated and pressurized reaction zone, in which zone, water in the feedstock has a temperature of
25 374°C or greater and a pressure of 22.1 MPa or greater and wherein the feedstock includes organic matter and contacting the feedstock with the catalyst in the reaction zone to yield a product containing water, hydrogen, methane, carbon dioxide or mixtures
30 thereof.

 Suitable organic matter feedstocks for use in methods according to the present invention include biomass, organic waste and mixtures thereof. Suitable reaction media include water, whether in
35 pure form or in a mixture with other substances, at

supercritical conditions that preferably are substantially free of oxygen.

The present invention achieves numerous advantages. Numerous types of feedstocks may be utilized, including organic wastes and biomass having a high moisture content. Hydrogen yields and conversion of carbon in the feedstock to gas are high even at high feedstock flow rates and concentrations. Virtually complete gasification is achieved in relatively short periods of time. The reaction product may be substantially free of tar or char, even when the feedstock has a high carbon concentration. The carbon-based catalyst is relatively inexpensive compared to other catalysts, is stable in the environment of a supercritical water medium and maintains activity over long periods of time.

BRIEF DESCRIPTION OF THE DRAWINGS

The invention will be better understood by reference to the appended figures wherein:

Figure 1 is a schematic diagram for a method according to the present invention for gasifying biomass in a supercritical water-containing medium; and

Figure 2 depicts tar yield from catalytic gasification of glucose in supercritical water at increasing reaction temperature.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The term "organic matter" as used herein will denote biomass, such as plant species, sewage sludge, agricultural or forestry waste, and organic waste such as organic solvents, organic acids and the like. Exemplary plant species include those having relatively high moisture contents such as water

hyacinth, banana tree, cattails, green alga, kelp or other aquatic species.

5 The phrase "critical point" as used herein refers to the thermodynamic state of a substance in which its liquid and gaseous phases co-exist in equilibrium at the highest possible temperature. For water, the critical point is a temperature of 647K (374°C) and a pressure of 221 bar (22.1 MPa).

10 The term "supercritical" refers to a thermodynamic state at conditions beyond those recognized as the "critical point" of a substance. Thus, pure water at the supercritical condition has a temperature greater than 374°C and a pressure greater than 22.1 MPa. At or above the critical conditions, 15 the density of water is a function of both temperature and pressure. Supercritical water acts as a dense gas with the solvation characteristics of a nonpolar organic. Thus, organic compounds and gases are completely miscible with it, but inorganic 20 substances such as salts are immiscible.

The term "nonoxidizing" as used herein refers to the condition of being substantially free of oxygen or air.

25 A method according to the present invention generally involves contacting organic matter in a supercritical water-containing medium with a catalyst to produce hydrogen, carbon dioxide and other desired gaseous species. According to the present invention, organic waste or biomass having a high water content 30 may be utilized as is for a feedstock or may be put in a form, e.g., a slurry with water, that facilitates adequate flow and contact with the catalyst. The feedstock is contacted with the catalyst at suitable temperature and pressure 35 conditions so that the water is at supercritical conditions. Preferably, the temperature is about

600°C and the pressure is 22.1 MPa or greater. Under these conditions, the organic matter in the feedstock is rapidly and virtually completely gasified to produce hydrogen and other gases such as methane or other hydrocarbons, carbon monoxide and carbon dioxide, e.g., from thermal decomposition of the organic matter. Typically, less than 1 wt% of the reaction product is in the form of tars or chars.

The gas phase of the reaction product may be separated from the rest of the reaction product by conventional gas-liquid separation techniques. To reduce any hazards of explosion, the gases may be cooled.

As will be appreciated by those of skill in the art, several thermodynamic paths may be followed in order to achieve supercritical conditions for water. For example, in a constant volume process, a feedstock containing a biomass and water mixture may be heated until supercritical conditions are reached.

Alternatively, a method according to the present invention can be carried out in a constant pressure reactor scheme such as illustrated in Figure 1. Generally, the reactor scheme includes a feedstock supply and a heated flow-type reactor housing a catalyst and capable of maintaining conditions associated with a supercritical reaction medium.

Before the feedstock is introduced, substantially deaerated water having little or no oxygen therein is fed into a reactor and then the pressure is increased to a desired level. A feedstock 12, e.g., a slurry of biomass and water, can then be supplied to the reactor scheme from a feeding system 14. Flow rate of the feedstock out of the feeding system 14 and to a reactor 16 is controlled, e.g., by a pump 18. Reactor 16, which may be a flow-type reactor, contains a heating zone

8 ID 0,5 cm // 48 cm ^{hänge}

20, containing catalyst bed 22 through which the feedstock flows. A suitable form for such a reactor is a metal tube (0.375 inch OD, 0.187 inch ID and 18.9 inches long) made of a material such as INCONEL 625. Catalyst bed 22 may occupy a substantial portion of the reactor, e.g., about two-thirds of the heating zone of the reactor. On either end of the catalyst bed 22, i.e., at the front and back ends of a tube reactor, an inert material such as alumina beads may be used to confine the catalyst to the heating zone and to minimize action of the carbon-containing catalyst as an adsorbent.

known-
vol.

9,4 cm³

Conditions within the reactor as the conversion proceeds may be monitored, such as via thermocouples, not shown, located along the length of and inside the reactor, and by other conventional means, such as pressure transducer 23.

Upon entry into heating zone 20, the feedstock is heated rapidly. For example, heating may be achieved by coils or resistance heater 24, or both, on the outside of the reactor. After the water in the feedstock reaches supercritical conditions, pyrolysis products of the feedstock contact catalyst bed 22 in the heating zone and decompose to gases.

The decomposition products then pass out of the reactor via line 26 and the pressure of the reactor effluent may be reduced from the supercritical condition to atmospheric, such as through a back pressure regulator 27. Separation of the reactor effluent into gaseous and liquid phases may be achieved by a conventional separator 28, if desired. Such a separator also provides a convenient point for sampling.

Hydrogen is produced at high pressure, avoiding considerable expense of compression needed for commercial use.

The transformation of feedstocks containing organic matter and water in a method according to the present invention involves a catalytic thermal decomposition mechanism such as pyrolysis, rather than oxidation, using a carbon-based catalyst. As a result, samples of the effluent are substantially free of tar or char, that is, has less than about 1 weight per cent of such substances, as measured by conventional analytical techniques. Because of the pyrolytic reaction mechanism, the reaction medium is desirably substantially free of oxygen.

Concentration ranges for the organic matter contacting the catalyst may be adjusted by altering any or all of the following: the feedstock composition, its flow rate into the reactor, or the amount of catalyst in the reactor. For example, for glucose, a concentration up to about 22 wt% in water may be utilized. Also, a given type of biomass, as a whole or only certain portions, may be fed to the reactor, as collected or may be ground into a slurry before introduction into the reactor. In addition, the feedstock may contain other components other than water that become part of the reaction medium but do not interfere with the decomposition at supercritical conditions.

Catalysts useful in the present invention are carbon-based materials such as charcoals and activated carbons having high surface areas. Desirably, surface areas are about 1000 m²/g. An exemplary charcoal is one based on wood or macadamia shell. Coconut shell or coal activated carbons are other useful types of carbon-based catalysts. The catalyst may be powdery or granular. A preferred coconut shell activated carbon is designated Type PE, a granular (12 x 30 mesh) activated carbon commercially available from Barnebey & Sutcliffe Co.

of Columbus, Ohio. Table I presents comparative data exemplifying the performance of these types of carbon catalysts in a method according to the present invention.

invol. 9,4 cm³t₂ : ~ 1 min

~ 0,5 - 0,8 g Catalyst. 11

12,96 g glucose / h

Table I
Glucose Gasification in Supercritical Water at
600°C, 34.5 MPa with Various Carbon Catalysts

Glucose Concentration	1.2 M	1.2 M	1.2 M	1.2 M
Glucose Flow Rate	1.0 ml/min	1.0 ml/min	1.0 ml/min	1.0 ml/min
Catalyst Type	coal activated carbon	coconut shell activated carbon	macadamia shell charcoal	spruce charcoal
WHSV	19.9 (g/hr)/g	22.2 (g/hr)/g	25.7 (g/hr)/g	17.6 (g/hr)/g
Gas Product Yield ^a				
H ₂	1.48	2.24	2.71	1.61
CO	2.34	0.79	0.54	1.19
CO ₂	1.45	3.09	1.09	2.66
CH ₄	1.04	1.23	3.18	0.92
C ₂ H ₄	0.002	0.0	0.002	0.01
C ₂ H ₆	0.29	0.35	0.27	0.33
C ₃ H ₆	0.002	0.0	0.003	0.01
C ₃ H ₈	0.13	0.13	0.11	0.11
Carbon conversion ^b	97%	103%	95%	97%
Tar yield ^c	0.066%	0.008%	0.046%	0.009%
pH of liquid sample	4	5	4	4
WHSV = weight hourly space velocity in g glucose/hr-g catalyst				
^a gas yield = mole of gas/mole of reactant				
^b carbon conversion = mole of carbon in gas/mole of carbon in reactant				
^c tar yield = gram of dried residue/gram of reactant				

The time of exposure of the feedstock to the catalyst is generally that which is sufficient to effect virtually complete gasification. However, the time over which contact with the catalyst is carried out may be adjusted to take into account variations in the composition of the feedstock, and pressure and temperature of the supercritical water medium. For example, the dimensions of the conversion zone can be altered, e.g., by fabricating the reactor of tubes of relatively larger

or smaller diameters, in order to reduce or extend residence times.

Factors influencing efficient conversion of organic matter, such as biomass and organic waste, in a feedstock and
5 production of desirably high gas yields include reaction temperature, residence time and feedstock concentration. Tables II through IX set forth the results of a number of tests
run to provide guidelines useful in carrying out the present invention. Since glucose mimics the reaction chemistry of many
10 carbohydrates that, together with lignin, compose biomass, it serves as a suitable model for the study of thermochemical conversion of carbohydrates, as presented in several of the following Tables.

Table II presents the results of a study of glucose
15 gasification, with and without an activated carbon catalyst. As can be seen from this table, for the same glucose concentration, the conversion of carbon in the feedstock to gaseous product increases considerably by carrying out the gasification reaction over a carbon-containing catalyst such as
20 activated carbon according to the present invention. Significantly, even when WHSV was increased six-fold from 3.7 to 22.2 (g/hr)/g, complete carbon conversion was obtained, confirming the activity and efficiency of the carbon-containing catalysts in the present invention.

Table II
Glucose Gasification Over Activated Carbon Catalyst
In Supercritical Water at 600°C, 34.5 MPa

Gas Product Yield ^a	1.2 M glucose (no catalyst) res. time = 34 s	1.2 M glucose (with 0.60 g catalyst) WHSV = 22.2 (g/hr)/g	1.0 M glucose (with 2.77 g catalyst) WHSV = 3.7 (g/hr)/g
H ₂	0.56	2.24	1.73
CO	3.18	0.79	1.32
CO ₂	0.29	3.09	2.54
CH ₄	0.84	1.23	1.10
C ₂ H ₄	0.03	0.0	0.001
C ₂ H ₆	0.20	0.35	0.33
C ₃ H ₆	0.00	0.0	0.005
C ₃ H ₈	0.00	0.13	0.19
Carbon Conversion ^b	80%	103%	103%
WHSV = weight hourly space velocity in g glucose/hr-g catalyst Catalyst = coconut shell activated carbon ^a gas yield = mole of gas/ mole of reactant ^b carbon conversion = mole of carbon in the gas/ mole of carbon in the reactant			

Table III shows the effect of the ratio of the amount of glucose feedstock and that of the catalyst on gaseous product yield. Increasing the flow rate of feedstock relative to the catalyst, i.e., WHSV, hydrogen and carbon monoxide yields increase. Carbon conversion was very high.

Table III
Effect of WHSV on Gasification of 1.0 M Glucose Reactant
Over Activated Carbon Catalyst in
Supercritical Water at 600°C, 34.5 MPa

Gas Product Yield ^a	WHSV=3.7 (g/hr)/g	WHSV=6.6 (g/hr)/g	WHSV=13.5 (g/hr)/g
H ₂	1.73	1.57	1.97
CO	1.32	2.33	2.57
CO ₂	2.54	1.42	1.54
CH ₄	1.10	1.01	0.90
C ₂ H ₄	0.001	0.003	0.008
C ₂ H ₆	0.33	0.29	0.25
C ₃ H ₆	0.005	0.001	0.009
C ₃ H ₈	0.19	0.14	0.11
Carbon Conversion ^b	103%	96%	98%
WHSV = weight hourly space velocity in g glucose/hr-g catalyst Catalyst = coconut shell activated carbon ^a gas yield = mole of gas/ mole of reactant ^b carbon conversion = mole of carbon in the gas/ mole of carbon in the reactant			

Figure 2 illustrates that tar yield from the gasification of 1.0 M glucose is also a function of temperature. The lowest tar yield was obtained at 600°C while tar yield at 500°C was more than ten times higher.

Generally, process conditions should be such that the water in the reaction medium is at supercritical conditions. Table IV shows the effect of reaction temperature on glucose conversion. All of the temperatures were in the supercritical range. Pressure and WHSV were held constant. The highest carbon conversion and hydrogen yield were obtained at 600°C and tar yields were very low for each run at the different supercritical temperatures tested. More significantly, carbon conversion increased from 51% to 98% and hydrogen yields increased dramatically as the temperature was increased from 550°C to 600°C.

Table IV
Effect of Temperature on Gasification of 1.0 M Glucose
Reactant Over Activated Carbon Catalyst
in Supercritical Water (WHSV=13.5 (g/hr)/g)

Gas Product Yield ^a	600°C 34.5 MPa	550°C 34.5 MPa	500°C 34.5 MPa
H ₂	1.97	0.62	0.46
CO	2.57	1.67	1.57
CO ₂	1.54	0.73	0.85
CH ₄	0.90	0.37	0.25
C ₂ H ₄	0.008	0.01	0.016
C ₂ H ₆	0.25	0.10	0.07
C ₃ H ₆	0.009	0.03	0.04
C ₃ H ₈	0.11	0.05	0.036
Tar yield ^b	0.013	0.009	0.001
Carbon Conversion ^c	98%	54%	51%

WHSV = weight hourly space velocity in g glucose/hr-g catalyst

Catalyst = coconut shell activated carbon

^a gas yield = mole of gas/ mole of reactant

^b Tar yield = gram of dried residue/gram of reactant

^c carbon conversion = mole of carbon in the gas/ mole of carbon in reactant

Table V shows the effect of reaction pressure on glucose conversion. As can be seen, the highest carbon conversion and hydrogen yield were obtained at 34.5 MPa.

Table V Effect of Pressure on Gasification of 1.0 M Glucose Over Activated Carbon Catalyst in Supercritical Water at 600°C		
Gas Product Yield ^a	WHSV=3.7 (g/hr)/g 34.5 MPa	WHSV=9.3 (g/hr)/g 25.5 MPa

5	H ₂	1.73	1.18
	CO	1.32	2.47
	CO ₂	2.54	1.30
	CH ₄	1.10	0.86
	C ₂ H ₄	0.001	0.0081
	C ₂ H ₆	0.33	0.25
	C ₃ H ₆	0.005	0.014
	C ₃ H ₈	0.19	0.012
	Carbon Conversion ^b	103%	92%
10	<p>WHSV = weight hourly space velocity in g glucose/hr-g catalyst Catalyst = coconut shell activated carbon ^a gas yield = mole of gas/ mole of reactant ^b carbon conversion = mole of carbon in the gas/ mole of carbon in the reactant</p>		

- 15 Table VI sets forth results of the gasification of cellobiose, a dimer of glucose. Superior hydrogen yield and carbon conversion were obtained during the first three hours of operation, after which some catalyst deactivation was observed.

5

Table VI Gasification of Cellobiose Over Activated Carbon Catalyst In Supercritical Water at 600°C, 34.5 MPa			
0.235M cellobiose with 2.975 g activated carbon catalyst WHSV=1.92 (g/hr)/g			
Time on Stream (minutes)	53	192	237
Product	Gas Yield ^a		
H ₂	5.22	2.88	2.47
CO	1.59	1.83	1.49
CO ₂	7.30	6.62	5.53
CH ₄	1.87	1.96	1.40
C ₂ H ₄	0.001	0.003	0.002
C ₂ H ₆	0.47	0.48	0.34
C ₃ H ₆	0	0	0
C ₃ H ₈	0.19	0.20	0.12
Carbon Conversion ^b	102%	100%	79%
WHSV = weight hourly space velocity in g glucose/hr-g catalyst Catalyst = coconut shell activated carbon ^a gas yield = mole of gas/ mole of reactant ^b carbon conversion = mole of carbon in the gas/ mole of carbon in the reactant			

10

15

20

Table VII sets forth results of gasification of other biomass feedstocks, depithed bagasse liquid extract and water hyacinth. Nearly a third of the product from the bagasse extract was hydrogen and carbon conversion was high.

Table VII Gasification of Depithed Bagasse Liquid Extract and of Water Hyacinth Over Activated Carbon Catalyst in Supercritical Water at 600°C, 34.5 MPa	
----------------------------------------------------------------------------------------------------------------------------------------------------------------	--

15.5 g/l Depithed Bagasse Liquid Extract With 3.003 g Catalyst WHSV=0.32 (g/hr)/g			2.32 g/l Water Hyacinth With 2.77 g Catalyst WHSV = 0.05 (g/hr)/g	
Product	Gas Yield ^a	Mole Fraction ^b	Gas Yield ^a	Mole Fraction ^b
H ₂	2.3	32.8	2.8	22
CO	1	1	45	25
CO ₂	83	54	85	31
CH ₄	7	11	16	16
C ₂ H ₄	0	0	0	0
C ₂ H ₆	1.2	1	8.7	4.7
C ₃ H ₈	0	0	0	0
C ₃ H ₆	0.3	0.2	4.5	1.6
Total Gas Yield ^c	95%	--	162%	--
WHSV = weight hourly space velocity in g liquid extract/hr-g catalyst Catalyst = coconut shell activated carbon ^a gas yield = gram of gas/gram of reactant ^b Mole fraction = mole of gas/total mole gas in effluent ^c Total Gas Yield = gram of all gases/gram of reactant				

Table VIII sets forth results of gasification of sewage sludge. As can be seen, carbon catalysts can be effective in the thermal decomposition of such materials.

Table VIII
Gasification of Sewage Sludge Over Activated Carbon Catalyst
In Supercritical Water at 600°C, 34.5 MPa

28 g/l Sewage Sludge With 2.96 g Catalyst
WHSV = 0.5 (g/hr)/g

Product	Gas Yield ^a	Mole Fraction ^b
H ₂	2.7	33
CO	3.5	2.9
CO ₂	66.2	36
CH ₄	16.3	24
C ₂ H ₄	0.05	0.04
C ₂ H ₆	7.7	5.7
C ₃ H ₆	0.3	0.15
C ₃ H ₈	1.7	0.89
Total Gas Yield ^c	98.4†	--

WHSV = weight hourly space velocity in g glucose/hr-g catalyst
Catalyst = coconut shell activated carbon

^a gas yield = gram of gas/ gram of reactant

^b mole fraction = mole of gas/total mole of gas in effluent

^c Total Gas Yield = grams of all gases/gram of reactant

Table IX shows that carbon-containing catalysts as used in a method according to the present invention effectively treat organic wastes such as methanol, methyl ethyl ketone, ethylene glycol and acetic acid. Hydrogen yields and carbon conversion were very high.

V2: ~1 min

20

Table IX				
Catalytic Destruction of Representative Military Wastes over 2.824g Activated Carbon Catalyst in Supercritical Water at 600°C, 34.5 MPa				
WHSV (g/hr)/g	1.0M Methanol 0.76 1.15g/min	0.1M Methyl Ethyl Ketone 0.17	0.1M Ethylene Glycol 0.16	0.1M Acetic Acid 0.14
	Gas Product Yield ^a			
H ₂	1.61	2.97	1.27	1.08
CO	0.23	0.53	0.29	0.19
CO ₂	0.42	0.61	0.78	0.96
CH ₄	0.22	1.10	0.61	1.02
C ₂ H ₄	0.0	0.0	0.0	0.0
C ₂ H ₆	0.0	0.28	0.14	0.01
C ₃ H ₆	0.0	0.0	0.0	0.0
C ₃ H ₈	0.0	0.01	0.0	0.0
Carbon Conversion ^b	88%	71%	98%	111%
	Liquid Product			
Unconverted Reactant	6.8%	2.2%	0	0
WHSV = weight hourly space velocity in g waste/hr-g catalyst Catalyst = coconut shell activated carbon ^a gas yield = mole of gas/mole reactant ^b carbon conversion = mole of carbon in the gas/mole of carbon in the reactant				

While the present invention is disclosed by reference to the preferred embodiments and examples set forth above, it is to be understood that these examples are intended in an illustrative rather than a limiting sense. It is contemplated that modifications will readily occur to those skilled in the

art, which modifications will be within the spirit of the invention and within the scope of the appended claims.

CLAIMS

What is claimed is:

1. A method, comprising the step of contacting a feedstock in a reaction medium with a carbon-containing catalyst for a time sufficient to decompose the feedstock, wherein the feedstock comprises organic matter and the medium comprises water at a pressure of 22.1 MPa or greater and a temperature of 374 °C or greater.
2. A method according to Claim 1, wherein the catalyst comprises an activated carbon.
3. A method according to Claim 1, wherein the catalyst comprises a charcoal.
4. A method according to Claim 1, wherein the decomposition occurs at about 600°C.
5. A method according to Claim 1, wherein the organic matter is selected from the group consisting of biomass, organic waste and mixtures thereof.
6. A method according to Claim 1, wherein the reaction medium is substantially free of oxygen.
7. A method, comprising the step of contacting a feedstock in a supercritical water-containing medium with a

carbon-containing catalyst under conditions sufficient to gasify the feedstock, the feedstock comprising organic matter.

8. A method according to Claim 7, wherein the catalyst comprises an activated carbon.

5 9. A method according to Claim 7, wherein the catalyst comprises a charcoal.

10. A method according to Claim 7, wherein gasification occurs at about 600°C.

11. A method according to Claim 7, wherein the organic
10 matter is selected from the group consisting of biomass, organic waste and mixtures thereof.

12. A method according to Claim 7, wherein the medium is
substantially free of oxygen.

13. A method, comprising the steps of:

- 15 a) providing a catalyst in a reaction zone, the catalyst comprising carbon;
- b) preheating and pressurizing the reaction zone;
- c) introducing a water-containing feedstock into the preheated and pressurized reaction zone, wherein the feedstock
20 comprises organic matter and in which zone, the feedstock has a

temperature of 374°C or greater and a pressure of 22.1 MPa or greater; and

d) contacting the feedstock with the catalyst in the reaction zone to produce a product, the product comprising
5 water, hydrogen, methane, carbon dioxide or mixtures thereof.

14. A method according to Claim 13, wherein the catalyst comprises an activated carbon.

15. A method according to Claim 13, wherein the catalyst comprises a charcoal.

10 16. A method according to Claim 13, wherein the product is produced at about 600°C.

17. A method according to Claim 13, wherein the organic matter is selected from the group consisting of biomass,
organic waste and mixtures thereof.

15 18. A method according to Claim 13, wherein the reaction zone is substantially free of oxygen.

19. A method, comprising the steps of:

introducing into a reactor a mixture, the mixture comprising water and organic matter and the reactor housing a carbon-containing catalyst;

5 increasing the temperature and pressure conditions within the reactor to cause the pressure of the mixture to be at least 22.1 MPa and the temperature of the mixture to be at least 374°C and to pyrolyze the organic matter; and recovering an effluent from the reactor.

10 20. A method according to Claim 19, wherein the catalyst comprises an activated carbon.

21. A method according to Claim 19, wherein the catalyst comprises a charcoal.

15 22. A method according to Claim 19, wherein the product is produced at about 600°C.

23. A method according to Claim 19, wherein the organic matter is selected from the group consisting of biomass, organic waste and mixtures thereof.

24. A method according to Claim 19, wherein the reaction zone is substantially free of oxygen.

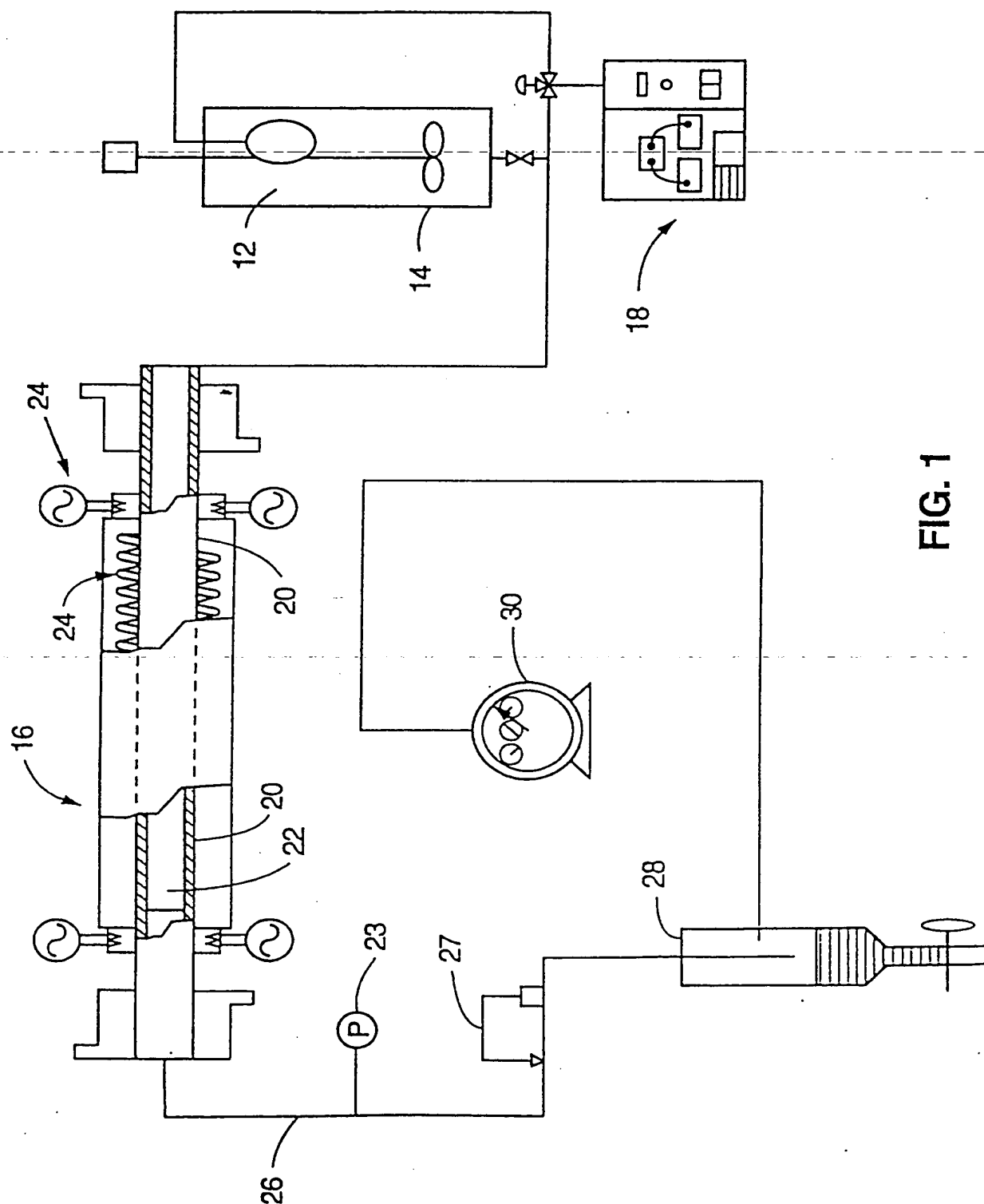


FIG. 1

2/2

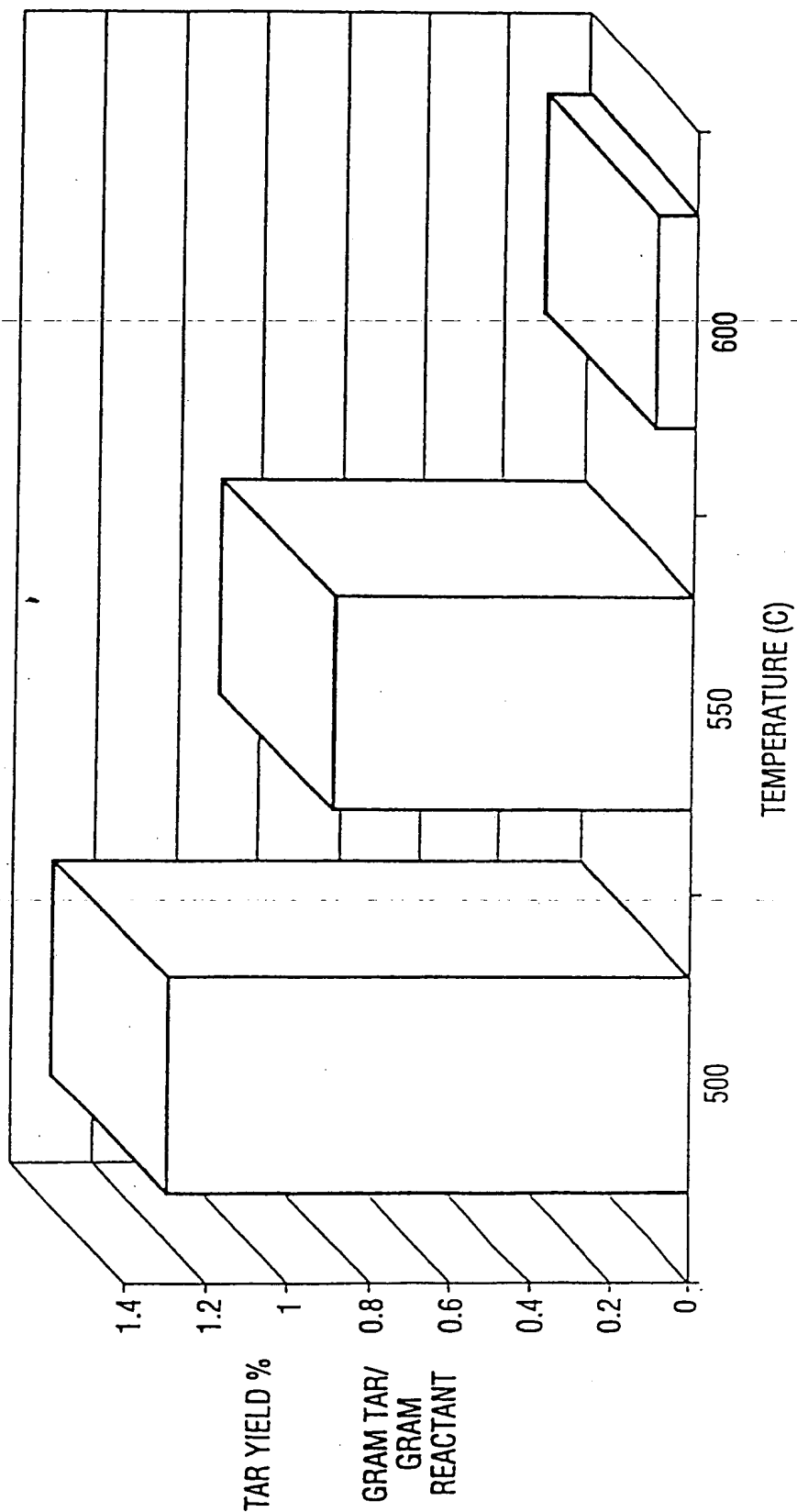


FIG. 2

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/04439

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C10J 3/00

US CL :48/197R, 202, 209; 423/648.1; 252/373

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : Please See Extra Sheet.

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US,A, 4,113,446 (MODELL ET AL.) 12 September 1978, See entire document.	1-24
Y, P	US,A, 5,460,792 (ROSENBAUM) 24 October 1995; see entire document.	1-24
Y	US,A, 4,558,027 (MC KEE ET AL.) 10 December 1985, see entire document.	1-24
Y	US,A, 2,880,167 (KIMBERLIN, JR. ET AL.) 31 March 1959, see entire document.	1-24
Y	US,A, 2,592,603 (SANFORD ET AL.) 15 April 1952, see entire document.	1-24
Y	US,A, 4,425,256 (PILIPSKI) 10 January 1984, see entire document.	1-24

☒ Further documents are listed in the continuation of Box C.
 ☐ See patent family annex.

* Special categories of cited documents:	*T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*Z* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

19 JUNE 1996

Date of mailing of the international search report

23 JUL 1996

 Name and mailing address of the ISA/US
 Commissioner of Patents and Trademarks
 Box PCT
 Washington, D.C. 20231

Facsimile No. (703) 305-3230

Authorized officer

PETER F. KRATZ

Telephone No. (703) 305-0196

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US96/04439

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

[illegible]

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US96/04439

B. FIELDS SEARCHED

Minimum documentation searched

Classification System: U.S.

48/197R, 202, 209, 214A, Dig. 7; 210/762, 774; 252/373; ; 423/648.1, 652, 445; 585/240, 241; 588/226, 228, 230;
502/180, 418